

Alexandrite From Lake Manyara, Tanzania*

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Introduction

The far-flung emerald deposit at Lake Manyara was mentioned by THURM (1972) and described more precisely by BANK (1974), by the present author (1973 & 1974), and more recently by MWAKISUNGA (1976). BANK (1974) reported a small piece of mother rock, on which, associated with feldspar and mica, alexandrite, emerald and ruby occurred, i.e. three extremely rare gemstones all of which owe their color to an admixture of chromium. From the mineral paragenesis he also surmised that the Manyara deposit was analogous to the famous occurrence of beryllium minerals at Tokowaya in the Ural mountains (described by FERSMANN, 1929), where the same gem minerals are found in close association. Towards the end of his paper "The Emerald Deposit at Lake Manyara, Tanzania" (*Lap. Journ.*, May, 1974) the writer refers to several other gems such as apatite, garnet, spinel and chrysoberyl, of which the detection of

alexandrite is the most intriguing (*Figure 1*).

Since then further investigation could be carried out on the alexandrite from Lake Manyara in its quality as a crystal and precious stone as well as on its mode of occurrence, justifying a special publication on this fascinating gem.

The mother rock of the Manyara alexandrite has meanwhile been carefully analyzed. Each individual mineral component was X-rayed. The red grains which can easily be seen in the rock all proved to be chondrodite. In thin sections they are yellow. Contrary to the previous information (GÜBELIN, 1974), garnet seems to be rather scarce or then very sparsely dispersed; at least it has not been encountered in a more recent and more thorough analysis. The mineral components which were definitely identified are in sequence of frequency: actinolite, enstatite, fayalitic olivine, chondrodite, chrysotile and pleonaste. Consequently the name *actinolite-schist* is proposed. In contrast to the former conjecture it is not a peridotite, be-

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cause it does not contain enough olivine. The association of actinolite and alexandrite indicate a metamorphic rock, hence: it is a schist.

According to BANK (1976) and OKRUSCH (1971) the possibilities of formation are more limited for the alexandrite than for ordinary chrysoberyl. Alexandrite owes its great rarity to the fact that the geochemical conditions are highly accidental because beryllium and chromium do not normally occur within the same rock suites. Beryllium is concentrated in the pegmatitic and pneumatolytic phases which themselves are devoid of chromium. The latter, on the other hand, is

more frequently present in mafic rocks. Therefore the formation of alexandrite may only be expected in places where the ingredients of these rocks can meet, that is to say, where the pegmatitic and pneumatolytic residual phases carry the beryllium into contact with the chromium in such ultramafic rocks as actinolite, peridotite, pyroxenite, and their metamorphic derivatives (particularly serpentinites). These were the favorable conditions found in the deposit at Lake Manyara manifesting close similarity to the deposit of Tokowaya as well as of the Girdlestone Farm at Novello, Rhodesia (BANK, 1964).

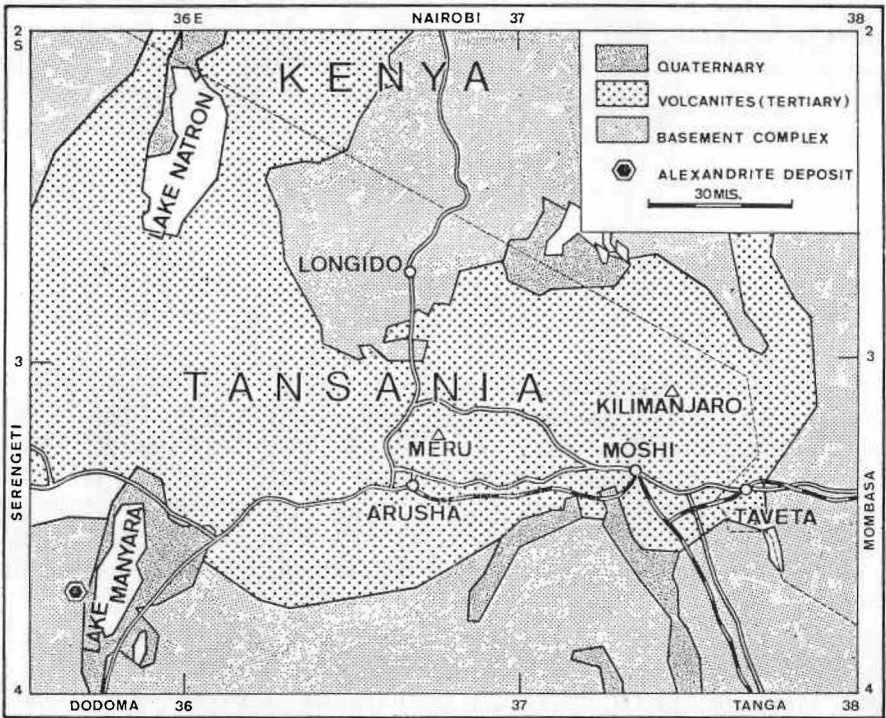


Figure 1. This simplified geological map of northern Tanzania shows the situation of the alexandrite deposit at Lake Manyara, where alexandrite occurs together with some other chromium-bearing gem minerals.

External Appearance

Considering this geochemical similarity of occurrence, the author was not astonished to observe that all the Manyara alexandrites which he has seen so far looked puzzlingly similar to those from Tokowaya and from Novello. In daylight they all displayed the same exquisite bluish-green hue with a remarkable change of color to pronounced raspberry red in incandescent light.

With a few exceptions, most of the specimens seen or investigated displayed those characteristic formations of three crystals intersecting each other, which yield the well known trillings. The habit of the individual crystal was mainly determined by the prism. Some were just broken-off crystals and others merely fragments. Some were absolutely clear and of exceptional gem quality and when cut would have resulted in high grade precious gems up to 5 carats. However, many crystals and fragments were intensely etched and marred by too many mineral and liquid inclusions as well as cracks.

Chemical Composition

By means of the electron microprobe, an analysis was carried out on two crystals, the results of which are communicated in *Table I*. The calculation program was started off in assuming BeO to amount to 20% (theoretical value), because due to the low atomic number ($Z=4$) of Be the microprobe does not register this element. In the alexandrite from Novello BeO amounts to 19% and thus very closely approaches the theoretical value.

TABLE I

	Alexandrite	
	No. 1	No. 2
	%	%
Be O	20	20
Al ₂ O ₃	77	78
Cr ₂ O ₃	0.25	0.20
Fe ₂ O ₃	0.7	0.7
V ₂ O ₃	—	—
Ti O ₂	0.12	0.08
Si O ₂	0.13	0.4

The percentage of the trace elements present reveals that chromium and iron are responsible for the color. Vanadium seems to be entirely absent. However, as will be explained further down, the striking alexandrite effect is caused solely by chromium, while iron is of secondary importance and mainly acting as an inhibitor (see later).

Physical Properties

The physical properties do not manifest any peculiarities — the one exception of course being the chameleon color change — and may therefore be mentioned hereafter merely for statistic purposes.

Density:

The frequency medium of numerous measurements taken results in

$$d = 3.71\text{g/cm}^3 \text{ at } 4^\circ\text{C}$$

R. I. and birefringence:

Again the medium data of numerous readings are:

$$\begin{aligned}n_\alpha &= 1.745 \\n_\beta &= 1.750 \\n_\gamma &= 1.754\end{aligned}$$

whereas the birefringence varied from 0.008 to 0.010. The optical character is of course negative.

Trichroism:

This property is very distinct and depending upon the three main optical directions produces the colors shown in Table II.

TABLE II

Optical direction	Daylight	Incandescent light
n_α	reddish	carmine red
n_β	yellow green	orange red
n_γ	blue green	greenish

For this accentuated pleochroism the transition-metal chromium alone is responsible.

Absorption:

The absorption spectrum is a typical chromium spectrum whose spectral image is characterized by two prominent bands and marked by several individual absorption lines in the red region (Figure 2). The two bands are designated A and B. They range astride the critical wavelengths of 580 nm and 415 nm. If they trespass these values the alexandrite is green, otherwise it is red. The A band extends from approximately 550 nm to roughly 610 nm and culminates at 571.4 nm. It is accompanied on its long-wave side by the telltale chromium lines at 680,

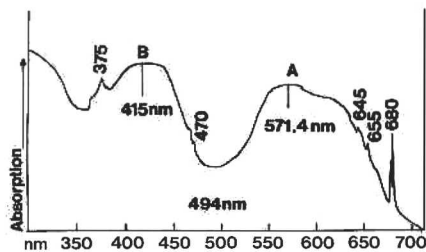


Figure 2. Absorption spectrum of the alexandrite from Lake Manyara in unpolarized light ranging from 325 nm to 700 nm at room temperature.

678, 665, 655, 649, and 645 nm which result from spin-forbidden transitions. The B band is somewhat narrower ranging from 395 nm to 443 nm with its peak at 415 nm. It is chaperoned by four satellite lines at 470 nm and 465 nm on the long-wave side and at 385 nm and 375 nm on the short-wave side. The latter two lines are caused by trivalent iron. The narrow lines in the red and in the short-wave section become more conspicuous when a polaroid is used. The absorption minimum is situated at 494 nm and very closely corresponds to the intensity maximum of the solar spectrum in the green (at 500 nm) imparting the alexandrite a green color in daylight. Incandescent light excels in a predominance of longer wavelengths which are transmitted by the alexandrite's second absorption minimum at 725 nm thus conferring the gem a red appearance.

The breadth of band A suggests that it must be provoked by two overlapping absorption spectra of two differing color centers. This becomes evident when polarized light is applied. In unpolarized light the breadth of the A band complex is produced by the superposition of two bands with maxima slightly displaced against each other. The polarized absorption parallel to the z-direction ($A_{\parallel z}$) culminating in longer wavelengths at 571.4 nm is responsible for the green color, while the polarized absorption perpendicular to the z-direction ($A_{\perp z}$) sweeps to a maximum among shorter wavelengths at 551 nm and induces red coloration (Figure 3). This change of color is called "Alexandrite Effect."

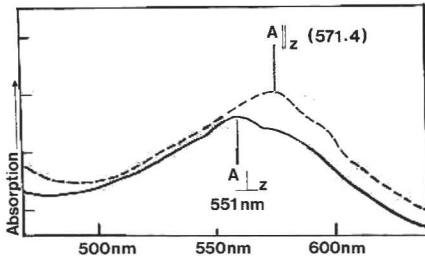


Figure 3. Polarized absorption spectra of band A parallel and perpendicular to the z-direction (Hassan *et al.*, 1974).

The alexandrite-effect:

This phenomenon is an exceptionally well-pronounced specialty of the Manyara alexandrite, for the color change from green to red and vice versa is very definite and so complete, that the beholder cannot help wondering about the nature of its cause. The attempt to explain essence and cause of this unusual feature was undertaken in numerous publications. For a very long time it was simply connected with the mineral's strong trichroism and it was merely regarded as an effect provoked solely by the different spectral composition of daylight and incandescent light. None of these older and rather one-sided explanations of the very complex process were convincing. Nowadays the contexts are better understood, and hence the interpretation of the causal conditions acquire a new significance. Today's apprehension is based upon a much more profound comprehension of the intrinsic structure of the alexandrite. While POOL (1964) and partly also WHITE *et al.* (1974) attributed the color change to a rather psychological effect of the human eye and brain than to the inherent structure and properties of the alexandrite, FARRELL *et al.* (1963 & 1965), NEWN

HAM *et al.* (1964), WHITE *et al.* (1967), and HASSAN *et al.* (1974) investigated the structural background of the question. Their results provide an instructive insight into the mechanisms which take place, when light falls into an alexandrite. The author feels that his present account of the Manyara alexandrite might be a welcome opportunity of making some integrating reflections on these more recent studies.

Alexandrite is isostructural with olivine and sinhalite, i.e. it has an identical structure as these two minerals (FARRELL, NEWNHAM, 1965 and STRUNZ 1968). The structure of the alexandrite is determined by a dense packing of the relatively large oxygen ions in a hexagonal arrangement. Within this lattice the tetrahedral interstices are occupied by Be while the Al partly sits inside the coordination octahedra. This results in a combination of tetrahedral BeO_4 groups and octahedral AlO_4 groups. Numerous chemical analyses as well as recent refinements of the structure of chrysoberyl have lead to the conviction that the transition element chromium (Cr^{3+}) (NASSAU, 1975) is the chromophorous ion, yet not vanadium. The aforementioned chemical analyses did not furnish any alibi for the existence of vanadium.

It is not the mere presence of Cr^{3+} ions within the structure of the alexandrite which is responsible for the color change but rather their array in the crystal lattice. Within the structure of the chrysoberyl there are various lattice sites with octahedral symmetry, which are held by Cr^{3+} instead of Al^{3+} ions. However, normally only two of

them are being claimed by Cr^{3+} . The refinement of the structure of chrysoberyl by FARRELL *et al.* (1963) disclosed that these two octahedral lattice sites preferred by the Cr^{3+} ions differ with regard to size – not very much but significantly enough to produce the color change (Figure 4). Half of the Al^{3+} ions are perched in coordination polyhedra with inversion symmetry = Al^{3+} (1) and the other on mirror plane positions = Al^{3+} (2). The average distances to the nearest oxygen ions measure 1.890Å for the Al^{3+} (1) sites and 1.934Å for the Al^{3+} (2) sites (the mean value between the two (= 1.914Å) happens to be almost identical to the distance $\text{Al} - \text{O}$ in alpha-corundum). If trivalent cations replace others they favor one place to another depending upon symmetry and size.

The Cr^{3+} ion ($\phi = 0.615\text{\AA}$) is slightly larger than the Al^{3+} ion ($\phi = 0.530\text{\AA}$) and hence prefers the more spacious Al^{3+} (2) sites. Yet, if introduced under pressure and high temperature some Cr^{3+} ions may accommodate themselves on narrower Al^{3+} (1) sites. The dispersion of the Cr^{3+} ions onto transition-metal sites differing in size and symmetry within the crystal field cannot happen without drastic influence on the color properties of the alexandrite, especially so because the absorption spectrum of the alexandrite consist of two individual spectra of the Cr^{3+} (1) and the Cr^{3+} (2) color centers overlapping one another in the A band.

The intrinsic cause of the chameleon effect of the Cr^{3+} ions on their two different lattice sites is their dif-

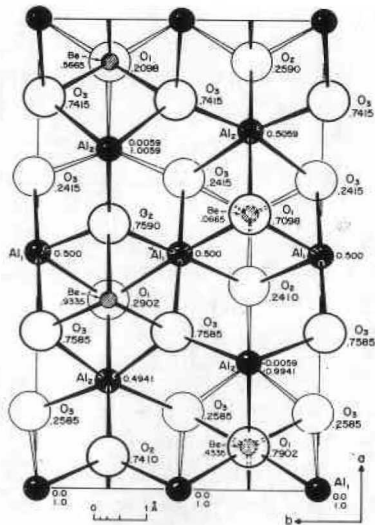


Figure 4. The refined structure of chrysoberyl projected on (001). Heights of the atoms are expressed in cell fractions (Farrell *et al.*, 1963).

ferent distance to the oxygen ions. On the smaller octahedral sites (1) of the alexandrite lattice the $\text{Cr} - \text{O}$ distance is shorter, the Cr^{3+} ion finds itself in a compressed position and thus promotes the transposition of the absorption maximum from 571.4 nm (assigned to the more numerous Cr^{3+} (2) centers) to 551 nm (ascribed to the less populated Cr^{3+} (1) centers). The denser the population of the Cr^{3+} (1) centers the greater the spectral dislocation and hence the more intense the red coloration. This condition concurs exactly with observations made in gemstones of the ruby type (ruby, spinel) where the red color also results from compressed space at the Cr^{3+} lattice sites.

The investigation of the two different coordination sites elucidates that the Cr^{3+} (1)/ Cr^{3+} (2) population ratio decides the color itself as well as

the intensity of the color change. The greater the $\text{Cr}^{3+} (1)/\text{Cr}^{3+} (2)$ ratio the more pronounced is the color of the alexandrite in daylight as well as in incandescent light. Due to the denser population of the $\text{Cr}^{3+} (2)$ centers, but also because of the polarizing influence of the adjacent Be ion acting as a central ion, the conditions for the Cr^{3+} ions are very similar as in the Cr^{3+} doped silicates of the emerald type (emerald, demantoid, hiddenite etc.) as long as the alexandrite is impelled by the intensity as well as by the spectral character of the light in which the gem is being viewed. Daylight or any other white illumination with an identical distribution of wavelengths interacts with both Cr^{3+} centers imparting the green as well as the red hue in dependence on the $\text{Cr}^{3+} (1)/\text{Cr}^{3+} (2)$ population ratio. In incandescent light on the other hand, which is relatively poor in short (blue, high energy) wavelengths but rich in long (red, low energy) wavelengths the alexandrite appears red, because the strong band B with its culmination at 415 nm absorbs the majority of the scanty short wavelengths up to about 443 nm thus blotting out almost all of the blue region. The residual light is being controlled by the broad A band complex at 571.4 nm, i.e. it absorbs mainly in the green. On account of its complex nature the band A also blacks out parts of the bluish green and of the yellowish green between 625.5–516.6 nm. This extensive absorption of almost all the shorter wavelengths results in the complementary purplish red color: the characteristic raspberry red of the alexandrite in incandescent light. From this it may

be concluded that the smaller the $\text{Cr}^{3+} (1)/\text{Cr}^{3+} (2)$ population ratio, i.e. the more concentrated the Cr^{3+} centers, the more important the absorption effect of band A.

After all these reflections it must, however, be considered that the A band complex is neither the sole nor the principal factor for the quality of the color change but rather the correlation of both bands A and B. Above all the absorbance of band B, that is to say, the sum of the absorbing centers in band B must apparently reach a certain critical value to completely absorb the shorter blue and green wavelengths which are in any way quite scanty in incandescent light.

In summarizing it may be recapitulated that the alexandrite effect materializes in that chromoforous chromium atoms in the state as Cr^{3+} ions occupy octahedral coordination sites in the crystal which are otherwise held by Al^{3+} ions. These sites differ in size; some of them are of normal largeness, others are constricted. The color change is provoked when in comparison to the $\text{Cr}^{3+} (2)$ ions on regular spacious sites sufficient Cr^{3+} ions can slip onto the compressed sites $\text{Cr}^{3+} (1)$, that is when a certain critical value of the $\text{Cr}^{3+} (1)/\text{Cr}^{3+} (2)$ ratio is reached. The distribution of the Cr^{3+} ions onto the different transition-metal sites certainly depends upon the growth conditions of the alexandrite; in order to force enough Cr^{3+} ions onto the compressed lattice sites either very high temperatures and low pressures or low temperatures with high pressures are necessary. Such extreme conditions happened to occur very rarely in the birth chambers of

the alexandrite (not to mention the extreme rarity of the chromium) so that natural specimens with a good color change are purely accidental!

The foregone explanation may be preliminary and perhaps it is an oversimplification but it had to be adapted to different grades of scientific education of the readers. To understand the miracle does not deny its existence!

In the above considerations the iron was not mentioned because it exerts no influence on the alexandrite effect. If present in sufficient quantity as to affect the color by imposing its absorption upon that of the chromium, Fe^{3+} may impair the purity of the hues in day and incandescent light. Thus iron is often responsible for the brownish tint of some alexandrites from Sri Lanka. In addition, iron acts as a powerful inhibitor in that it

prevents the alexandrite from emitting luminescence.

Behavior under short wave radiation:

Table I reveals that iron participates with 0.7% of the total amount of chemical elements in the composition of the Manyara alexandrite. This is approximately three times that of chromium. Yet, it appears to be insufficient for completely suppressing the luminescence, for contrary to alexandrites from other sources which are normally inert to shortwave illumination, the Manyara alexandrite glows faintly in UV light but does not respond to X-rays. This distinct luminescence serves as a welcome virtue of distinction from (a) genuine alexandrites from other deposits and (b) both types of synthetic alexandrite presently known. *Table III* offers a clear survey of the behaviour under



Figure 5. A "parcel" of dark blackish brown biotite flakes (32x).

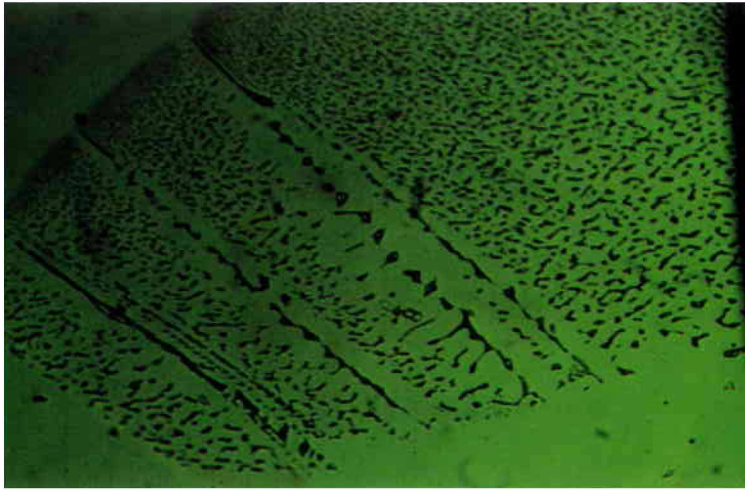


Figure 6. A section of a "fingerprint" inclusion, i.e. a partially healed fracture marked by a system of intercommunicating channels of residual liquid (40x).

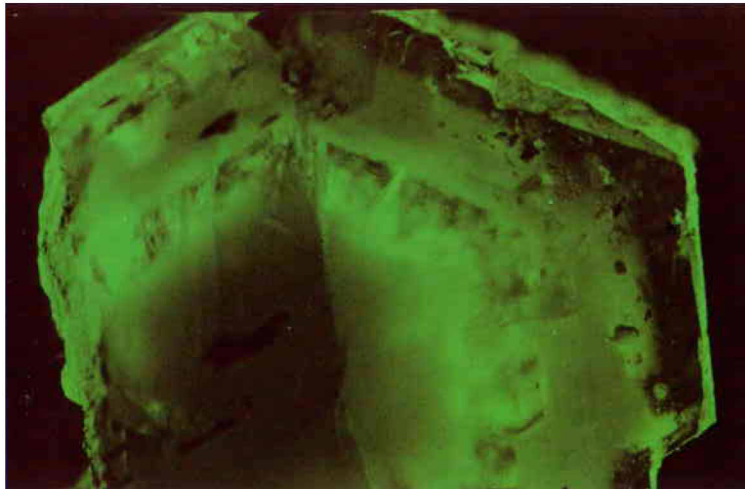


Figure 7. Pseudohexagonal arrangement of color zones alternatively dark and pale green (32x).

short wave radiation of the various genuine and synthetic alexandrites.

The immediate deduction to be assumed from the positive response of the Manyara alexandrite to UV radiation would be that it contains less iron than the alexandrites from the other localities. This observation is also confirmed by the high degree of transmission of the Manyara alexandrite in long wave UV light. Under short wave UV radiation all natural alexandrites as well as flux grown synthetic alexandrites are opaque, while the Czochralski pulled synthetic alexandrites are transparent.

Inclusions

The internal paragenesis of the Manyara alexandrite is typically moulded by its mode of formation and the component minerals of the mother

rock. Therefore it is not surprising to encounter some minerals of the external mineral association such as actinolite and biotite. The actinolite occurs in the form of fibres or stalks either discretely distributed or then concentrated in irregular masses or as slightly divergent sheaves. Close and dense arrangement of fine actinolite fibres may cause chatoyancy in some specimens. The biotite also either assembles in the well known form of so-called "books" or hovers as individual flakes in the body of its host gem (*Figure 5*). In one small alexandrite an individual, well formed crystal of apatite was observed.

The majority of those Manyara alexandrites excelling in inclusions contain mainly fanciful liquid inclusions which traverse the whole crystal

TABLE III

ALEXANDRITE FROM:	LUMINESCENCE			Transparency in long wave UV light 365 nm	Opacity in short wave UV light 254 nm
	long wave UV light 365 nm	short wave UV light 254 nm	X-Rays		
Lake Manyara Tanzania	medium dull red	weak yellowish	inert	good	opaque
Novello Rhodesia	inert	inert	inert	medium	opaque
Ratnapura Sri Lanka	inert	inert	inert	medium	opaque
Tokowaya Ural Mts. Siberia	inert	inert	inert	medium	opaque
<u>Synthetic Alexandrite</u>					
flux grown (Patterson)	distinct orange red	very weak reddish	inert	very good	opaque
Czochralski pulled (Dr. Morris)	strong red	strong red	inert	excellent	transparent

at random and display the characteristic appearance of secondary inclusions or partly healed fractures. Their pattern is decided by liquid filled tubes or channels which are more loosely disseminated or then by dense and irregular arrangement of ramifying veins and capillaries (Figure 6). No small number of Manyara alexandrites display periodic growth either by a layered distribution of the color or a pseudohexagonal zonal accord of light and darker shades (Figure 7).

Unfortunately the supply of this magnificent precious stone from Lake Manyara will presumably always remain rather uncertain or at least very irregular and in any case too scarce as to satisfy a receptive market, and the exorbitant prices which were asked from the beginning did not help to promote the gem's popularity.

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